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Patent Office



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[General Power]

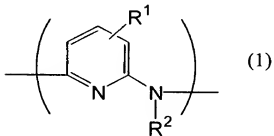
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[Document Name] Claims

[Claim 1]

Polyaminopyridines having a structural unit represented by the following general formula (1);



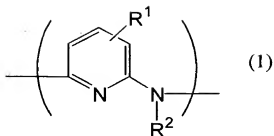
(wherein R^1 represents a hydrogen atom, an alkyl group of a carbon number of 1 to 10, a hydroxyl group, an alkanoyl group, a carbamoyl group or a cyano group, and R^2 represents a phenyl group optionally having a substituent or a pyridyl group optionally having a substituent) and having a number average molecular weight in a range of 500 to 1000000.

[Claim 2]

The polyaminopyridines according to claim 1, wherein R^1 is a hydrogen atom, and R^2 is a phenyl group or a pyridyl group in the general formula (1).

[Claim 3]

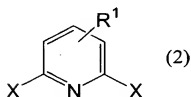
A process for preparing polyaminopyridines having a structural unit represented by the following general formula (1);



(wherein R^1 represents a hydrogen atom, an alkyl group of a carbon number of 1 to 10, and a hydroxyl group, an alkanoyl group, a carbamoyl group or a cyano group, and R^2 represents a phenyl group optionally having a substituent or a pyridyl group optionally having a substituent) and having a number average molecular weight in a range of 500 to 1000000,

which comprises reacting 2,6-dihologenopyridines

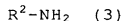
represented by the following general formula (2);



(wherein R^1 is as defined in the general formula (1), and X represents a halogen atom)

and an aromatic amine compound represented by the

following general formula (3);



(wherein R^2 is as defined in the general formula (1))

using a palladium compound and a phosphine compound as a mixed catalyst in the presence of a base.

[Document Name] Specification

[Title of the Invention] Polyaminopyridines and process
for preparing the same

[Technical Field]

5 [0001]

The present invention relates to
polyaminopyridines and a process for preparing the same.
More particularly, the present invention relates to novel
polyaminopyridines used in a cell active material, a
10 polymer-type organic electroluminescent material and the
like as conductive resin, and a process for preparing the
same.

[Background Art]

[0002]

15 Polyaminopyridines are utilized in
electromagnetic wave shielding materials, plastic
magnetics and the like, in addition to utilities utilizing
the electroconductive function such as condensers, static
electricity preventing agents, IC boards, electron beam IC
20 circuit patterning and the like, utility utilizing the
redox function such as batteries, electroluminescent
elements and the like, utility utilizing electronic device
function such as transistors, diodes, solar cells and the
like, utility utilizing optical function such as
25 photoconductive materials, high optical communication
elements (non-linear optical elements), optical computers
and the like.

[0003]

As such the polyaminopyridines, for example, polyaminopyridines obtained by oxidation-polymerizing aminopyridines are known (see Patent Publication 1).

However, since polyaminopyridines obtained by oxidation-polymerizing aminopyridine are a polymer in which pyridine rings are bound at a variety of positions, and the polymer is partially branched, and crosslinked, those polyaminopyridines have low solubility in a variety of solvents, and their utility is remarkably restricted.

Therefore, there is desired development of novel polyaminopyridines excellent in solubility in various solvents.

[Patent Publication 1] JP-A No.61-85440

[Disclosure of the Invention]

[Problem to be solved by the Invention]

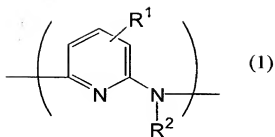
[0004]

An object of the present invention is to provide novel polyaminopyridines which are excellent in solubility in various solvents and a process for preparing the same.

[Means for solving the problem]

[0005]

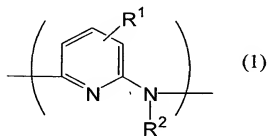
That is, the present invention relates to polyaminopyridines having a structural unit represented by the following general formula (1);



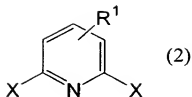
(wherein R^1 represents a hydrogen atom, an alkyl group of a carbon number of 1 to 10, a hydroxyl group, an alkanoyl group, a carbamoyl group or a cyano group, and R^2 represents a phenyl group optionally having a substituent or a pyridyl group optionally having a substituent) and having a number average molecular weight in a range of 500 to 1000000.

[0006]

Also, the present invention relates to a process for preparing polyaminopyridines having a structural unit represented by the following general formula (1);



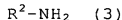
(wherein R^1 and R^2 are as defined above) and having a number average molecular weight in a range of 500 to 1000000, which comprises reacting 2,6-dihalogenopyridines represented by the following general formula (2);



(wherein R^1 is as defined in the general formula (1), and X represents a halogen atom)

and an aromatic amine compound represented by the

5 following general formula (3);



(wherein R^2 is as defined in the general formula (1)) using a palladium compound and a phosphine compound as a mixed catalyst in the presence of a base.

10 [Effect of the Invention]

[0007]

According to the present invention, novel polyaminopyridines which are excellent in solubility in a variety of solvents can be provided.

15 [Best Mode for carrying out the Invention]

[0008]

Polyaminopyridines of the present invention are a compound represented by the general formula (1).

In the general formula (1), R^1 represents a
 20 hydrogen atom, an alkyl group of a carbon number of 1 to 10, a hydroxyl group, an alkanoyl group, a carbamoyl group or a cyano group, and R^2 represents a phenyl group optionally having a substituent, a pyridyl group optionally having a substituent,

25 [0009]

Examples of the alkyl group of a carbon number of 1 to 10 include methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, n-pentyl group, isopentyl group, neopentyl group, n-hexyl group, isohexyl group, n-octyl group, n-decyl group and the like.

[0010]

Examples of the alkanoyl group include methanoyl group, ethanoly group and the like.

10 [0011]

Examples of the phenyl group optionally having a substituent include phenyl group, 2-methylphenyl group, 2-ethylphenyl group, 2-n-hexylphenyl group, 2-n-octylphenyl group, 2-n-decylphenyl group, 4-methylphenyl group, 4-ethylphenyl group, 4-n-hexylphenyl group, 4-n-octylphenyl group, 4-n-decylphenyl group, 2,4-dimethylphenyl group, 2,4-diethylphenyl group, 2,4-di-n-hexylphenyl group, 2,4-di-n-octylphenyl group, 2,4-di-n-decylphenyl group, 2-hydroxyphenyl group, 2-methanoylphenyl group, 2-carbamoylphenyl group, 2-cyanophenyl group, 4-hydroxyphenyl group, 4-methanoylphenyl group, 4-carbamoylphenyl group, 4-cyanophenyl group and the like.

[0012]

25 Examples of the pyridyl group optionally having a substituent include 2-pyridyl group, 3-pyridyl group, 4-pyridyl group, 3-methyl-2-pyridyl group, 3-ethyl-2-pyridyl group, 3-n-hexyl-2-pyridyl group, 3-n-octyl-2-pyridyl

group, 3-n-decyl-2-pyridyl group, 5-methyl-2-pyridyl group, 5-ethyl-2-pyridyl group, 5-n-hexyl-2-pyridyl group, 5-n-octyl-2-pyridyl group, 5-n-decyl-2-pyridyl group, 2-methyl-3-pyridyl group, 2-ethyl-3-pyridyl group, 2-n-hexyl-3-pyridyl group, 2-n-octyl-3-pyridyl group, 2-n-decyl-3-pyridyl group, 4-methyl-3-pyridyl group, 4-ethyl-3-pyridyl group, 4-n-hexyl-3-pyridyl group, 4-n-octyl-3-pyridyl group, 4-n-decyl-3-pyridyl group, 6-methyl-3-pyridyl group, 6-ethyl-3-pyridyl group, 6-n-hexyl-3-pyridyl group, 6-n-octyl-3-pyridyl group, 6-n-decyl-3-pyridyl group, 3-methyl-4-pyridyl group, 3-ethyl-4-pyridyl group, 3-n-hexyl-4-pyridyl group, 3-n-octyl-4-pyridyl group, 3-n-decyl-4-pyridyl group, 5-methyl-4-pyridyl group, 5-ethyl-4-pyridyl group, 5-n-hexyl-4-pyridyl group, 5-n-octyl-4-pyridyl group, 5-n-decyl-4-pyridyl group, 3-hydroxy-2-pyridyl group, 3-methanoyl-2-pyridyl group, 3-carbamoyl-2-pyridyl group, 3-cyano-2-pyridyl group, 5-hydroxy-2-pyridyl group, 5-methanoyl-2-pyridyl group, 5-carbamoyl-2-pyridyl group, 5-cyano-2-pyridyl group, 2-hydroxy-3-pyridyl group, 2-methanoyl-3-pyridyl group, 2-carbamoyl-3-pyridyl group, 2-cyano-3-pyridyl group, 4-hydroxy-3-pyridyl group, 4-methanoyl-3-pyridyl group, 4-carbamoyl-3-pyridyl group, 4-cyano-3-pyridyl group, 6-hydroxy-3-pyridyl group, 6-methanoyl-3-pyridyl group, 6-carbamoyl-3-pyridyl group, 6-cyano-3-pyridyl group, 3-hydroxy-4-pyridyl group, 3-methanoyl-4-pyridyl group, 3-carbamoyl-4-pyridyl group, 3-cyano-4-pyridyl group, 5-hydroxy-4-pyridyl group, 5-methanoyl-4-pyridyl group, 5-

carbamoyl-4-pyridyl group, 5-cyano-4-pyridyl group and the like.

[0013]

Examples of polyaminopyridines of the present invention include poly(2-(N-phenyl)aminopyridine), poly(2-(N-phenyl)amino-4-methylpyridine), poly(2-(N-phenyl)amino-4-ethylpyridine), poly(2-(N-phenyl)amino-4-n-propylpyridine), poly(2-(N-phenyl)amino-4-n-butylpyridine), poly(2-(N-phenyl)amino-4-n-hexylpyridine), poly(2-(N-phenyl)amino-4-n-octylpyridine), poly(2-(N-phenyl)amino-4-n-decylpyridine), poly(2-(N-2-pyridyl)aminopyridine), poly(2-(N-2-pyridyl)amino-4-methylpyridine), poly(2-(N-2-pyridyl)amino-4-n-hexylpyridine), poly(2-(N-3-pyridyl)aminopyridine), poly(2-(N-3-pyridyl)amino-4-methylpyridine), poly(2-(N-3-pyridyl)amino-4-n-hexylpyridine), poly(2-(N-4-pyridyl)aminopyridine), poly(2-(N-4-pyridyl)amino-4-methylpyridine), poly(2-(N-4-pyridyl)amino-4-n-hexylpyridine), poly(2-(N-3-methyl-2-pyridyl)aminopyridine), poly(2-(N-2-methyl-3-pyridyl)aminopyridine), poly(2-(N-3-methyl-4-pyridyl)aminopyridine) and the like.

[0014]

A number average molecular weight of polyaminopyridines of the present invention is 500 to 1000000, preferably 1000 to 100000. When a number average molecular weight of polyaminopyridines is less than 500, there is a possibility that film forming property is

deteriorated upon coating or casting of the resulting solution. On the other hand, when a number average molecular weight exceeds 1000000, there is a possibility that solubility in a solvent is deteriorated.

5 [0015]

Examples of a process for preparing polyaminopyridines of the present invention include a process of reacting 2,6-dihalogenopyridines and an aromatic amine compound using a palladium compound and a phosphine compound as a mixed catalyst in the presence of a base.

[0016]

The 2,6-dihalogenopyridines are a compound represented by the general formula (2). In the general formula (2), R^1 is as defined in the general formula (1). And, X represents a halogen atom.

Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, an iodine atom and the like.

20 [0017]

Examples of 2,6-dihalogenopyridines represented by the general formula (2) include 2,6-difluoropyridine, 2,6-dichloropyridine, 2,6-dibromopyridine, 2,6-diiodopyridine, 3-methyl-2,6-dichloropyridine, 4-methyl-2,6-dichloropyridine, 5-methyl-2,6-dichloropyridine, 3-ethyl-2,6-dichloropyridine, 4-ethyl-2,6-dichloropyridine, 5-ethyl-2,6-dichloropyridine, 3-isopropyl-2,6-dichloropyridine, 4-isopropyl-2,6-dichloropyridine, 5-

isopropyl-2,6-dichloropyridine, 3-n-propyl-2,6-dichloropyridine, 4-n-propyl-2,6-dichloropyridine, 5-n-propyl-2,6-dichloropyridine, 3-n-butyl-2,6-dichloropyridine, 4-n-butyl-2,6-dichloropyridine, 5-n-butyl-2,6-dichloropyridine, 3-sec-butyl-2,6-dichloropyridine, 4-sec-butyl-2,6-dichloropyridine, 5-sec-butyl-2,6-dichloropyridine, 3-tert-butyl-2,6-dichloropyridine, 4-tert-butyl-2,6-dichloropyridine, 5-tert-butyl-2,6-dichloropyridine, 3-n-pentyl-2,6-dichloropyridine, 4-n-pentyl-2,6-dichloropyridine, 5-n-pentyl-2,6-dichloropyridine, 3-isopentyl-2,6-dichloropyridine, 4-isopentyl-2,6-dichloropyridine, 5-isopentyl-2,6-dichloropyridine, 3-neopentyl-2,6-dichloropyridine, 4-neopentyl-2,6-dichloropyridine, 5-neopentyl-2,6-dichloropyridine, 3-n-hexyl-2,6-dichloropyridine, 4-n-hexyl-2,6-dichloropyridine, 5-n-hexyl-2,6-dichloropyridine, 3-iso-hexyl-2,6-dichloropyridine, 4-iso-hexyl-2,6-dichloropyridine, 5-iso-hexyl-2,6-dichloropyridine, 3-n-octyl-2,6-dichloropyridine, 4-n-octyl-2,6-dichloropyridine, 5-n-octyl-2,6-dichloropyridine, 3-n-decyl-2,6-dichloropyridine, 4-n-decyl-2,6-dichloropyridine, 5-n-decyl-2,6-dichloropyridine, 4-cyano-2,6-dichloropyridine, 4-hydroxy-2,6-dichloropyridine and the like. Inter alia, from a viewpoint of easy availability and economy, 2,6-dichloropyridine and 2,6-dibromopyridine are preferably used.

[0018]

On the other hand, the aromatic amine compound is a compound represented by the general formula (3). In the general formula (3), R^2 is as defined in the general formula (1).

5 [0019]

Examples of the aromatic amine compound represented by the general formula (3) include aniline, 2-methylaniline, 2-ethylaniline, 2-n-hexylaniline, 2-n-octylaniline, 2-n-decylaniline, 4-methylaniline, 4-ethyl-
10 ethylaniline, 4-n-hexylaniline, 4-n-octylaniline, 4-n-decylaniline, 2-hydroxyaniline, 2-methanoylaniline, 2-carbamoylaniline, 2-cyanoaniline, 4-hydroxyaniline, 4-methanoylaniline, 4-carbamoylaniline, 4-cyanoaniline, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 4-methyl-
15 2-aminopyridine, 4-ethyl-2-aminopyridine, 4-n-hexyl-2-aminopyridine, 4-n-octyl-2-aminopyridine, 4-n-decyl-2-aminopyridine, 6-methyl-2-aminopyridine, 6-ethyl-2-aminopyridine, 6-n-hexyl-2-aminopyridine, 6-n-octyl-2-aminopyridine, 6-n-decyl-2-aminopyridine, 2-methyl-3-
20 aminopyridine, 2-ethyl-3-aminopyridine, 2-n-hexyl-3-aminopyridine, 2-n-octyl-3-aminopyridine, 2-n-decyl-3-aminopyridine, 4-methyl-3-aminopyridine, 4-ethyl-3-aminopyridine, 4-n-hexyl-3-aminopyridine, 4-n-octyl-3-aminopyridine, 4-n-decyl-3-aminopyridine, 6-methyl-3-
25 aminopyridine, 6-ethyl-3-aminopyridine, 6-n-hexyl-3-aminopyridine, 6-n-octyl-3-aminopyridine, 6-n-decyl-3-aminopyridine, 2-methyl-4-aminopyridine, 2-ethyl-4-aminopyridine, 2-n-hexyl-4-aminopyridine, 2-n-octyl-4-

aminopyridine, 2-n-decyl-4-aminopyridine, 6-methyl-4-aminopyridine, 6-ethyl-4-aminopyridine, 6-n-hexyl-4-aminopyridine, 6-n-octyl-4-aminopyridine, 6-n-decyl-4-aminopyridine, 4-hydroxy-2-aminopyridine, 4-methanoyl-2-aminopyridine, 4-carbamoyl-2-aminopyridine, 2-cyano-2-aminopyridine, 6-hydroxy-2-aminopyridine, 6-methanoyl-2-aminopyridine, 6-carbamoyl-2-aminopyridine, 6-cyano-2-aminopyridine, 2-hydroxy-3-aminopyridine, 2-methanoyl-3-aminopyridine, 2-carbamoyl-3-aminopyridine, 2-cyano-3-aminopyridine, 4-hydroxy-3-aminopyridine, 4-methanoyl-3-aminopyridine, 4-carbamoyl-3-aminopyridine, 4-cyano-3-aminopyridine, 6-hydroxy-3-aminopyridine, 6-methanoyl-3-aminopyridine, 6-carbamoyl-3-aminopyridine, 6-cyano-3-aminopyridine, 2-hydroxy-4-aminopyridine, 2-methanoyl-4-aminopyridine, 2-carbamoyl-4-aminopyridine, 2-cyano-4-aminopyridine, 6-hydroxy-4-aminopyridine, 6-methanoyl-4-aminopyridine, 6-carbamoyl-4-aminopyridine, 6-cyano-4-aminopyridine and the like. Inter alia, from a viewpoint of easy availability and economy, aniline, 2-aminopyridine, 3-aminopyridine, and 4-aminopyridine are preferably used.

[0020]

It is desirable that an amount of the aromatic amine compound to be used is 0.5 to 1.5 mole, preferably 0.9 to 1.1 mole per 1 mole of 2,6-dihalogenopyridines. When an amount of the aromatic amine compound to be used is less than 0.5 moles, there is a possibility that a reaction becomes difficult to proceed. On the other hand,

when an amount of the aromatic amine compound to be used exceeds 1.5 moles, the effect corresponding to a use amount is not exerted, and this is not economical.

[0021]

5 Examples of the palladium compound include a
tetraivalent palladium compound such as sodium
hexachloropalladate (IV) tetrahydrate, potassium
hexachloropalladate (IV) and the like; a divalent
palladium compound such as palladium (II) chloride,
10 palladium (II) bromide, palladium (II) acetate, palladium
acetylacetonate (II), dichlorobis(benzonitrile)palladium
(II), dichlorobis(acetonitrile)palladium (II),
dichlorobis(triphenylphosphine)palladium (II),
dichlorobis(tri-*o*-tolylphosphine)palladium (II),
15 dichlorotetraaminepalladium (II), dichloro(cyclooctane-
1,5-diene)palladium (II), palladium trifluoroacetate (II)
and the like; a zerovalent palladium compound such as
tris(dibenzylideneacetone)dipalladium (0),
tris(dibenzylideneacetone)dipalladium (0) chloroform
20 complex, tetrakis(triphenylphosphine)palladium (0) and the
like. Among them, from a viewpoint of high reaction
activity, a zerovalent palladium compound is preferable.
Inter alia, tris(dibenzylideneacetone)dipalladium (0) has
highest reaction activity, and is preferably used.

25 [0022]

It is desirable that an amount of the palladium
compound to be used is 0.01 to 20 mol%, preferably 0.02 to
5 mol% per 2,6-dihalogenopyridines in terms of palladium.

When an amount of the palladium compound to be used is less than 0.01 mol%, there is a possibility the reaction becomes difficult to proceed. And, when an amount of the palladium compound to be used exceeds 20 mol%, the effect corresponding to a use amount is not exerted and this is not economical.

[0023]

On the other hand, examples of the phosphine compound include a phosphine compound having the chelating ability as a bidentate ligand such as 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, 1,1'-bis(diphenylphosphino)ferrocene, N,N'-dimethyl-1-[1',2-bis(diphenylphosphino)ferrocenyl] and the like. Inter alia, from a viewpoint of high reaction activity, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl is preferably used.

[0024]

It is desirable that an amount of the phosphine compound to be used is 0.1 to 10 moles, preferably 0.5 to 5 moles per mole of the palladium compound. When an amount of the phosphine compound to be used is less than 0.1 moles, there is a possibility that the reaction becomes difficult to proceed. And, when an amount of the phosphine compound to be used exceeds 10 moles, the effect corresponding to a use amount is not exerted, and this is not economical.

[0025]

The palladium compound and the phosphine compound may be added alone to the reaction system, or may

be added as a mixed catalyst by preparing into a complex in advance.

Examples of the base used in the present invention include alkali metal alkoxide such as sodium methoxide, sodium ethoxide, potassium methoxide, potassium ethoxide, lithium-tert-butoxide, sodium-tert-butoxide, potassium-tert-butoxide and the like. These bases may be prepared from an alkali metal, alkali metal hydride and alkali metal hydroxide and an alcohol and may be added to the reaction system.

[0026]

It is desirable that an amount of the base to be used is 2 mole or more, preferably 2 to 10 mole per 1 mole of 2,6-dihalogenopyridines. When an amount of the base to be used is less than 2 moles, there is a possibility that a yield is reduced.

In the present invention, the reaction is performed in an inert solvent. Examples of the inert solvent include aromatic hydrocarbon solvents such as benzene, toluene, xylene and the like; ether solvents such as diethyl ether, tetrahydrofuran, dioxane and the like; acetonitrile, dimethylformamide, dimethylsulfoxide, hexamethylphosphotriamide and the like. Inter alia, since recycling of a solvent is easy, aromatic hydrocarbon solvents such as benzene, toluene, xylene and the like are preferably used.

[0027]

It is desirable that a reaction temperature is

20 to 250 °C, preferably 50 to 150 °C. When a reaction temperature is lower than 20 °C, there is a possibility that the reaction takes a long time. On the other hand, when a reaction temperature is higher than 250 °C, there is a possibility that a side reaction occurs, and a yield is reduced. A reaction time is different depending on a reaction temperature, and is usually 1 to 20 hours.

The thus obtained polyaminopyridines can be isolated, for example, by adding a mixed solvent of aqueous ammonia/methanol or the like to precipitate polyaminopyridines, filtering and washing them to remove a catalyst and the like, and drying this.

[Examples]

[0028]

The present invention will be specifically explained below by way of Examples, but the present invention is not limited to these Examples. A number average molecular weight of polyaminopyridines obtained in Examples was measured at 30 °C using gel permeation chromatography (GPC) eluted with N,N-dimethylformamide, and was calculated based on standard polystyrene.

[0029]

Example 1

A four-necked flask, of a volume of 1 L, equipped with a condenser and a thermometer was charged with 12.83 g (86.7 mmol) of 2,6-dichloropyridine, 8.06 g (86.7 mmol) of aniline, 1.98 g (2.16 mmol) of tris(dibenzylideneacetone)dipalladium (0), 4.05 g (6.50

mmol) of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, 25.00 g (260.1 mmol) of sodium-tert-butoxide and 800 mL of toluene. Then, a temperature was raised to 100 °C under the nitrogen atmosphere, and the mixture was reacted at 5 100 °C for 8 hours. After completion of the reaction, the reaction solution was cooled to room temperature, the reaction solution was added to 2 L of a mixed solvent of 28 wt% aqueous ammonia/methanol (volume ratio 1/4), and precipitates were filtered to obtain crude poly(2-(N-phenyl)aminopyridine). The resulting crude poly(2-(N-phenyl)aminopyridine) was washed with 0.5 L of a mixed solvent of 28 wt% aqueous ammonia/methanol (volume ratio 10 1/4), further washed with methanol, and dried under reduced pressure to obtain 14.49 g of poly(2-(N-phenyl)aminopyridine) as a brown powder (yield 99.5 %). A number average molecular weight of the resulting poly(2-(N-phenyl)aminopyridine) was 4500. 15 [0030]

The resulting poly(2-N-phenyl)aminopyridine) 20 had the following physical properties, and could be identified therefrom.

IR (KBr): 3058, 1568, 1494, 1415, 1351, 1261, 1157, 1072, 778, 730, 695 (cm⁻¹)

25 Elementary analysis (wt%)

Theoretical value C: 77.9 H: 4.8 N: 16.5 Cl:
0.8

Measured value C: 78.6 H: 4.7 N: 16.0 Cl:

0.7

[0031]

Example 2

According to the same manner as that of Example

1 except that an amount of

tris(dibenzylideneacetone)dipalladium (0) was changed to 0.99 g (1.08 mmol), and an amount of 2,2'-

bis(diphenylphosphino)-1,1'-binaphthyl was changed to 2.03 g (3.25 mmol) in Example 1, 12.65 g of poly(2-(N-

phenyl)aminopyridine) was obtained (yield 86.9 %). A number average molecular weight of the resulting poly(2-(N-phenyl)aminopyridine) was 5500.

[0032]

Example 3

According to the same manner as that of Example

1 except that 20.55 g (86.7 mmol) of 2,6-dibromopyridine was used in place of 12.83 g (86.7 mmol) of 2,6-

dichloropyridine in Example 1, 14.56 g of poly(2-(N-phenyl)aminopyridine) was obtained (yield 100 %). A number

average molecular weight of the resulting poly(2-(N-phenyl)aminopyridine) was 6500.

[0033]

Example 4

A four-necked flask, of a volume of 1 L,

equipped with a condenser and a thermometer was charged with 12.83 g (86.7 mmol) of 2,6-dichloropyridine, 8.16 g (86.7 mmol) of 2-aminopyridine, 1.98 g (2.16 mmol) of tris(dibenzylideneacetone)dipalladium (0), 4.05 g (6.50

mmol) of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, 25.00 g (260.1 mmol) of sodium-tert-butoxide and 800 mL of toluene. Then, a temperature was raised to 100 °C under the nitrogen atmosphere, and the mixture was reacted at 100 °C for 8 hours. After completion of the reaction, the reaction solution was cooled to room temperature, the reaction solution was added to 2 L of a mixed solvent of 28 wt% aqueous ammonia/methanol (volume ratio 1/4), and precipitates were filtered to obtain crude poly(2-(N-2-pyridyl)aminopyridine). The resulting crude poly(2-(N-2-pyridyl)aminopyridine) was washed with 0.5 L of a mixed solvent of 28 wt% aqueous ammonia/methanol (volume ratio 1/4), further washed with methanol and dried under reduced pressure to obtain 13.25 g of poly(2-(N-2-pyridyl)aminopyridine) as a brown powder (yield 90.4 %). A number average molecular weight of the resulting poly(2-(N-2-pyridyl)aminopyridine) was 3500.

[0034]

The resulting poly(2-(N-2-pyridyl)aminopyridine) had the following physical properties, and could be identified therefrom.
IR (KBr): 1645, 1597, 1557, 1434, 865, 701 (cm⁻¹)
Elementary analysis (wt%)

Theoretical value C: 70.3 H: 4.1 N: 24.6 Cl:

1.0

Measured value C: 71.0 H: 4.5 N: 23.4 Cl:

1.1

[0035]

Comparative Example 1 (process of Patent Publication 1)

A four-necked flask, of a volume of 1 L, equipped with a condenser and a thermometer was charged with 15.06 g (160 mmol) of 2-aminopyridine, 8.11 g (50 mmol) of iron chloride (FeCl_3) and 800 ml of toluene. Then, a temperature was raised to 100 °C under the nitrogen atmosphere, and the mixture was reacted at 100 °C for 6 hours. After completion of the reaction, the reaction solution was cooled to room temperature, and filtered to obtain crude polyaminopyridine, the resulting crude polyaminopyridine was washed with 2 L of a mixed solvent of 28 wt% aqueous ammonia/methanol (volume ratio 1/4), further washed with methanol, and dried under reduced pressure to obtain 12.60 g of polyaminopyridine as an ochreous powder (yield 83.67 %). Since the resulting polymer was not dissolved in N,N-dimethylformamide, a number average molecular weight could not be measured by GPC.

[0036]

Assessment

Solubility of polyaminopyridines obtained in Examples and a Comparative Example in various solvents was assessed. Polyaminopyridines were dissolved in tetrahydrofuran, toluene, xylene, dichloromethanes and water, respectively, to a resin concentration of 1 wt% and the state of the solution was observed visually. Complete dissolution was assessed as 0, incomplete dissolution was assessed as

Δ , and no dissolution was assessed as x.

[0037]

[Table 1]

	solvent				
	tetrahydrofuran	toluene	xylene	dichloromethane	water
Example 1	O	O	O	O	x
Example 2	O	O	O	O	x
Example 3	O	O	O	O	x
Example 4	Δ	Δ	Δ	Δ	O
Comparative					
Example 1	x	x	x	x	x

[0038]

5 From Table 1, it is seen that
polyaminopyridines obtained in Examples 1 to 3 are
dissolved in various organic solvents. And, it is seen
that polyaminopyridines obtained in Examples 4 are
dissolved in water. To the contrary, polyaminopyridine
10 according to the previous process was inferior in
solubility in any of tested solvents.

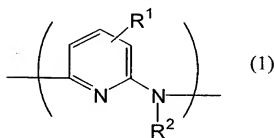
[Document Name] Abstract

[Abstract]

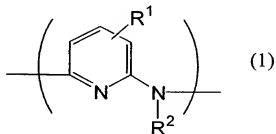
[Problem] To provide polyaminopyridines which are excellent in solubility in various solvents and a
 5 process for preparing the same.

[Means for solving the Problem]

Polyaminopyridines having a structural unit represented by the following general formula (1);

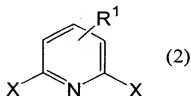


10 (wherein R¹ represents a hydrogen atom, an alkyl group of a carbon number of 1 to 10, a hydroxyl group, an alkanoyl group, a carbamoyl group or a cyano group, and R² represents a phenyl group optionally having a substituent or a pyridyl group optionally having a substituent)
 15 and having a number average molecular weight in a range of 500 to 1000000; and a process for preparing polyaminopyridines having a structural unit represented by the following general formula (1);

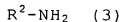


20 (wherein R¹ represents a hydrogen atom, an alkyl group of a

carbon number of 1 to 10, and a hydroxyl group, an alkanoyl group, a carbamoyl group or a cyano group, and R^2 represents a phenyl group optionally having a substituent or a pyridyl group optionally having a substituent) and
 5 having a number average molecular weight in a range of 500 to 1000000,
 which comprises reacting 2,6-dihalogenopyridines represented by the following general formula (2);



10 (wherein R^1 is as defined in the general formula (1), and X represents a halogen atom)
 and an aromatic amine compound represented by the following general formula (3);



15 (wherein R^2 is as defined in the general formula (1))
 using a palladium compound and a phosphine compound as a mixed catalyst in the presence of a base.

[Selected Drawing] None